



Propylene-Bridged Associative Bis(bipyridinium) Electrolytes for Long-Lifetime Aqueous Organic Redox Flow Batteries

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Abstract: Aqueous organic redox flow batteries (AORFBs) represent a potent technology in low-cost storage and grid-scale adoption of renewable electricity, whereas bipyridinium derivatives, the most extensively adopted anolyte, undergo diverse side reactions causing severe loss of battery lifetime. Here, we propose a strategy to promote the formation of intramolecular radical π dimers of reduced bipyridinium electrolytes and stabilize the radical intermediates during charge and discharge, resulting in significant improvements in battery lifetime. Density functional theory calculations reveal that proof-of-concept electrolytes, M-bisV and TMAP-bisV, demonstrate Gibbs free energy change of $-101.49 \text{ kJ mol}^{-1}$ and $-103.90 \text{ kJ mol}^{-1}$ for the formation of radical π dimers, as opposed to the less favored $-14.36 \text{ kJ mol}^{-1}$ for methyl viologen. Electron paramagnetic resonance and UV-vis spectra studies confirmed the significantly facilitated intramolecular π - π stacking of M-bisV and TMAP-bisV radicals. This translates to a more than one order of magnitude improvement in electrolyte stability for M-bisV and TMAP-bisV in flow cells. Specifically, TMAP-bisV possesses a theoretical capacity of 66.5 Ah L^{-1} and exhibits negligible capacity fade at 1.5 M e^{-} , which represents a new record in this area. We believe the concept may open a promising avenue toward the design of capacity-dense and super-stable AORFB electrolytes.

Introduction

A majority of the current electricity supply is provided by power plants that consume large amounts of fossil fuels,

resulting in enormous CO_2 emissions and increasing concerns about environmental benignity.^[1] To counteract this situation, green electricity generated from renewable energy resources (represented by wind and solar energy) has developed rapidly.^[2] Nevertheless, the fluctuating nature of renewable energy makes it challenging to balance the intermittent supply and constant demand for green electricity, impeding the grid-scale adoption of renewable electricity.^[3] Therefore, stationary electrical energy storage systems are in urgent need. Aqueous redox flow batteries (ARFBs), which utilize redox reactions of electrochemically active electrolytes to store energy, are promising choices, considering the high safety, decoupled capacity and power, and easy scale-up.^[4–8]

Aqueous organic redox flow batteries (AORFBs) use water-soluble organic redox-active electrolytes that are composed of earth-abundant elements (C, H, O, N, etc.), standing as low-cost station energy storage solutions. There are many more electrolyte options with tunable performance and potentially low cost.^[9,10] The molecular engineering on organic electrolytes could provide an even larger landscape to explore. For example, quinones,^[11–14] bipyridiniums,^[15–21] allox-/phenazines,^[22–28] naphthalene diimides,^[29–32] fluorenones,^[33] and azobenzenes^[34] are reported as anolytes of AORFBs, whereas quinones,^[35,36] ferrocenes,^[37–40] nitroxide radicals,^[15,41–43] methylene blue,^[44,45] phenazines,^[46] and benzidines^[47] are developed as catholytes.

Among the various types of AORFBs, pH-neutral AORFBs adopt electroactive organic electrolytes dissolved in KCl or NaCl solutions (or purely water) instead of corrosive acidic^[11] or basic^[12] solutions, which alleviate undesired hydrogen or oxygen evolution reactions and demonstrate longer lifetimes.^[48] Bipyridiniums, represented by methyl viologen (MV) and derivatives, are the most extensively studied anolytes for pH-neutral AORFBs.^[49,50] In 2016, MV was adopted in pH-neutral AORFB by reducing MV to a cation radical ($\text{MV}^{+\bullet}$) through one electron transfer to store electricity.^[16] But the fragile radical may undergo bimolecular decomposition, which generates σ dimers, causing a high capacity fade rate of 0.58%–7.5% per day (even worse at a higher concentration) for MV-based pH-neutral AORFBs.^[50–53]

To mitigate side reactions, Beh et al. have designed BTMAP-Vi (1,1'-bis[3-(trimethylammonio)propyl]-4,4'-bipyridinium tetrachloride, also named as $(\text{NPr})_2 \text{ V}$) by introducing bulky quaternary ammonium groups, which alleviate the aggregation of radicals and lower the capacity

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 Supporting Information section

fade rate of 0.1 M BTMAP-Vi/BTMAP-Fc cell to 0.033% per day (by a factor of ~ 20 than that of MV).^[17,54] Liu et al. employed α -cyclodextrin (α -CD) as an additive to suppress bipyridinium radical aggregation, resulting in a capacity fade rate of 0.12% per day for a 0.1 M EV+ α -CD/FcNEBr cell.^[55] More recently, Carrington et al. reported the intermolecular associative interactions between π -extended bipyridinium radicals to contribute an exBP/4-OH-TEMPO cell with robust battery performance even in air.^[20]

Although the development of bipyridiniums has made great advancements, bipyridiniums still face challenges caused by the parasitic side reactions associated with free radical intermediates and their aggregation, particularly at higher concentrations.^[50,55–58] Moreover, compared with MV, the reported molecular engineering strategies often provided enhanced battery lifetime at the cost of high molecular weight, leading to low specific capacity. Hydrophobic functional groups also decrease the solubility of bipyridiniums, resulting in low volumetric capacity. For example, the molecular weight and capacity of MV are 257 and 67.0 Ah L⁻¹, respectively, whereas they are 500 and 53.6 Ah L⁻¹ for BTMAP-Vi^[17] or 576 and 34.8 Ah L⁻¹ for exBP.^[20,59] Thus, it remains a challenge to design bipyridiniums that can offer both high capacity and long battery life.

Here, we report a strategy of designing associative bis(bipyridinium) electrolytes to facilitate the intramolecular π - π stacking of free radical intermediates by limiting the entropic (ΔS) freedom of bipyridinium moieties. The intramolecular associative interactions between free radicals are associated with large Gibbs free energy change (ΔG) values of less than -100 kJ mol⁻¹, which significantly raises the energy barrier for electrolyte decomposition. To demonstrate, we calculated, designed and synthesized two bis(bipyridinium) electrolytes, including 1',1'''-(propane-1,3-diyl)bis(1-methyl-[4,4'-bipyridine]-1,1'-diium) tetrachloride, namely M-bisV, and 1',1'''-(propane-1,3-diyl)bis(1-(3-(trimethylammonio)propyl)-[4,4'-bipyridine]-1,1'-diium) hexachloride, namely TMAP-bisV, in which two bipyridinium moieties are covalently linked by a propylene group. Density functional theory (DFT) calculations revealed the facilitated intramolecular π - π stacking of M-bisV and TMAP-bisV radicals with ΔG values of -101.49 kJ mol⁻¹ and -103.90 kJ mol⁻¹, respectively, in sharp contrast to values for the intermolecular π - π stacking of MV (-14.36 kJ mol⁻¹) and BTMAP-Vi (0.67 kJ mol⁻¹) radicals, and we found that the major contribution stems from the limited freedom of radical moieties, i.e., $-\Delta S$. Comprehensive cyclic voltammetry (CV), UV-vis, and electron paramagnetic resonance (EPR) studies were conducted to explore the electrochemical properties and intramolecular π - π stacking of free radical intermediates. Our results show that M-bisV and TMAP-bisV can undergo two reversible one-electron-transfer reactions with fast rate constants, with a high theoretical capacity of 63.8 and 66.5 Ah L⁻¹ at a molecular weight of 263 and 383 per electron storage, respectively. We confirm that the free radical intermediates of M-bisV and TMAP-bisV during charge-discharge can bind strongly with each other, which suppresses side reactions and improves battery life. This leads to energy-dense and long-life pH-neutral AORFBs. In 0.5 M

e⁻ flowing full cells, M-bisV and TMAP-bisV demonstrated remarkably low capacity fade rates of 0.10% per day and 0.014% per day, respectively, in contrast to that of MV (2.81% per day) and BTMAP-Vi (1.02% per day) when paired with FcNCl ((ferrocenylmethyl)trimethylammonium chloride^[37]). Particularly, TMAP-bisV, with a theoretical capacity of 66.5 Ah L⁻¹, demonstrated negligible capacity fade at 1.5 M e⁻ and stands as the most stable form of bipyridinium electrolytes for AORFBs. We anticipate our strategy may be broadly applicable in exploring novel organic electrolytes for high-performance AORFBs, where the intramolecular electrolyte interactions in solution play a decisive role.

Results and Discussion

Bipyridinium and relevant derivatives, represented by MV, have been extensively adopted as the primary anolyte of pH-neutral AORFBs. They normally get one electron from the electrode when charged, yielding a cationic radical intermediate that tends to form intermolecular π dimers with ΔG value of -14.8 kJ mol⁻¹ (Figure 1a).^[60] The reactive cationic radical intermediates can also form intermolecular σ dimers, causing fast degradation of battery capacity with capacity fade rates ranging from 0.58% to 7.5% per day for MV-based AORFBs.^[49–53] To prevent intermolecular side reactions, Beh et al. devised BTMAP-Vi^[17] (known also as (NPr)₂V^[54]) by grafting a bulky and charged end group to increase electrostatic repulsion between intermediate radicals, which lowers the battery capacity fade rate to 0.033% per day, by a factor of ~ 20 than that of MV at 0.1 M (Figure 1a). Nevertheless, BTMAP-Vi radical dimers can still be observed,^[56] especially in a more concentrated solution. The concentration-dependent degradation of bipyridinium radicals was also observed by Liu et al., who employed α -CD to stabilize and form a host-guest complex with ethyl viologen radicals, realizing a capacity fade rate of 0.12% per day at 0.1 M for the EV+ α -CD/FcNEBr cell, which exacerbates to 0.32% per day when the electrolyte concentration is raised to 0.5 M.^[55,61] In contrast to the aforementioned perceptions, Carrington et al. proposed that the formation of π dimers is not detrimental to battery lifetime, but instead can be utilized to construct robust pH-neutral AORFBs, even in open-air, by increasing the closed-shell characteristics and promoting the intermolecular associative interaction of reduced π -extended bipyridiniums. (Figure 1a).^[20] Although great efforts have been devoted to alleviating the side reactions of reduced bipyridiniums during AORFB operation (at the cost of increasing molecular weight and decreasing capacity), previous strategies failed to deliver energy-dense AORFBs and the stability of bipyridiniums (especially at higher concentrations > 0.5 M) necessitates further improvement. It is particularly critical to understand and regulate the chemical/electrochemical behavior of bipyridinium radicals.

Herein, we propose a strategy of designing associative bis(bipyridinium) electrolytes to promote the intramolecular π - π stacking of bipyridinium radicals. We speculate that bis(bipyridinium) electrolytes can undergo two one-electron reductions, yielding covalently-bonded radicals, which could

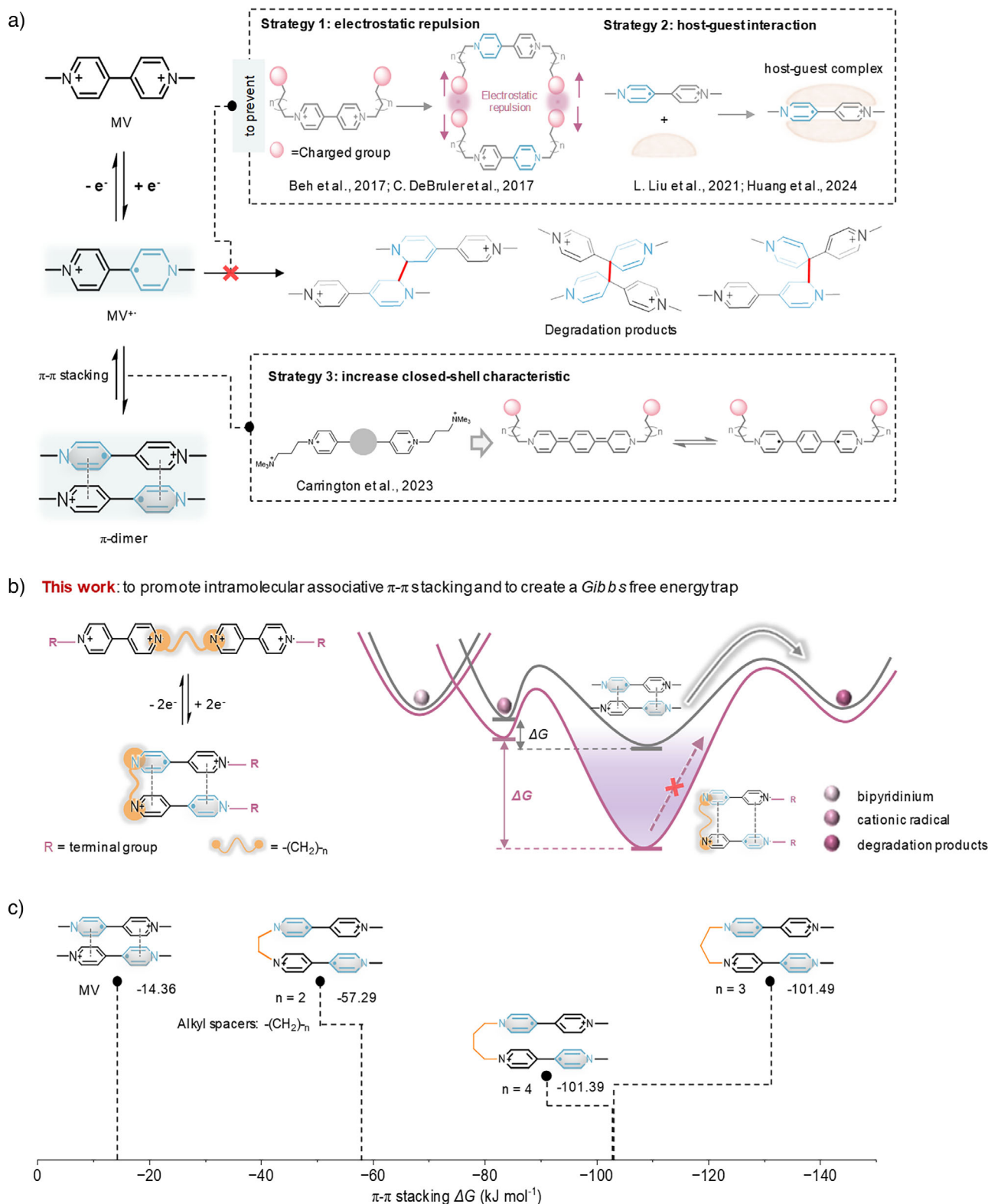


Figure 1. Design of intramolecularly associative bis(bipyridinium) electrolytes for AORFB. a) Reversible redox reactions of bipyridinium anolyte (represented by methyl viologen, MV) generate cationic radicals, which could cause side reactions during battery cycling and also undergo π - π stacking in solution. Previous strategies to improve AORFB performance include (1) electrostatic repulsion to mitigate bimolecular side reactions, (2) host-guest interaction to protect free radicals, and (3) increasing closed-shell characteristics to stabilize bipyridinium electrolytes. b) Electrolyte design strategy of this work by promoting the intramolecular associative π - π stacking through bonding two bipyridiniums and creating a Gibbs free energy well to stabilize the free radical intermediates. c) Density functional theory (DFT) calculated Gibbs free energy change (ΔG) for the formation of associative radical π dimers from cationic free radicals linked with alkyl spacers having varied lengths ($-(CH_2)_n$, $n = 2, 3, 4$).

Table 1: Electrochemical and physicochemical properties of electrolytes.

Electrolyte	$E_{1/2}^a$ (V vs SHE)	D^b ($\text{cm}^2 \text{s}^{-1}$)	Capacity ^c (Ah L^{-1})	k_0^d (cm s^{-1})	Solubility ^e (mol L^{-1})	Permeability ^f ($\text{cm}^2 \text{s}^{-1}$)
M-bisV	−0.29	3.18×10^{-6}	63.8	1.30×10^{-2}	1.19	4.86×10^{-13}
TMAP-bisV	−0.25	2.58×10^{-6}	66.5	1.60×10^{-2}	1.24	1.68×10^{-13}
MV ^[64]	−0.44	5.7×10^{-6}	67.0	3.3×10^{-3}	2.5	1.19×10^{-11}
BTMAP-Vi ^[62]	−0.36	3.07×10^{-6}	53.6	6.86×10^{-3}	2.0	3.14×10^{-13}

^a $E_{1/2}$, redox potential of one-electron reduction of bipyridinium moieties. ^b D , diffusion coefficient; D of M-bisV and TMAP-bisV was determined by diffusion-ordered spectroscopy. ^c Theoretical capacity. ^d k_0 , electron-transfer rate constant of one-electron reduction of each bipyridinium groups.

^e Solubility in water. ^f Permeability of the electrolytes across a Selmemion AMVN membrane.

transform into an intramolecular π dimer with low ΔG . Consequently, a deep Gibbs free energy well of bis(bipyridinium) radicals is generated, resulting in a very high energy barrier for the subsequent decomposition side reactions (Figure 1b). This strategy is in contrast to the concept proposed by Carrington et al. and the intramolecular π – π stacking of bis(bipyridinium) radicals (as well as the capacity fade caused by side reactions of intermediate radicals) may not depend on concentrations.^[52]

To prove our assumptions, several bis(bipyridinium) structures are designed with alkyl spacers of varied lengths and presented in Figure 1c. Our DFT calculations show bis(bipyridinium)s linked by a propylene bridge demonstrate the lowest ΔG value and the most appropriate conformation for the formation of intramolecular π dimers (Figure S1). Impressively, bis(bipyridinium) electrolytes exhibit significantly lower ΔG values than that of MV^[58,60] (a DFT calculated value of $-14.39 \text{ kJ mol}^{-1}$, Figure S1a, supported by an experimental value of $-14.8 \text{ kJ mol}^{-1}$). This implies the inclination of intramolecular over intermolecular π – π stacking after linking two bipyridiniums and verifies our design concept. Additionally, in Figure 1c, these bis(bipyridinium) electrolytes possess molecular weight (per electron) of 256–270, which is comparable to that of MV (257), indicating the unique advantage of our strategy.

As the proof of concept, two bis(bipyridinium) electrolytes with the optimized structure, namely M-bisV and TMAP-bisV, were synthesized as presented in Figure 2a. All products were confirmed by ^1H NMR and mass spectrometry (Figures S2–S4). MV and BTMAP-Vi were also synthesized according to reported procedures and served as controls (Figures S5 and S6).

M-bisV and TMAP-bisV exhibited two reversible redox reactions, with the first positioned at -0.29 and -0.25 V versus SHE (the standard hydrogen electrode, Figures 2b and S7 and Table 1), respectively. By contrast, the measured first redox potential of MV and BTMAP-Vi is -0.44 and -0.36 V versus SHE, respectively, which is more negative than that of M-bisV and TMAP-bisV. Interestingly, we found the potential difference between the first-electron and the second-electron redox reactions for TMAP-bisV is 0.52 V, which is larger than that of BTMAP-Vi (0.35 V),^[59] along with a more negative second-electron redox potential for TMAP-bisV (Figure S7e). This indicates that the lowest unoccupied molecular orbital (LUMO) of TMAP-bisV radicals has a higher energy than that of BTMAP-Vi radicals.^[59,62] Our DFT calculations reveal that the LUMO energy of separated TMAP-bisV radicals is

-3.35 eV, lower than that of BTMAP-Vi radicals (-2.80 eV), whereas the intramolecularly associative π – π stacking interaction of TMAP-bisV radicals increases the LUMO energy to -2.63 eV. We observed a narrow peak-to-peak separation (ΔE_p) of 30 and 35 mV for M-bisV and TMAP-bisV, respectively, which is consistent with two-electron-transfer process. Considering the redox potentials, this is a concurrent two one-electron-transfer process. These results and calculations suggest that the radicals of singly-reduced M-bisV and TMAP-bisV may undergo intramolecular π – π stacking as depicted in Figure 2a.

We prove the two one-electron-transfer processes of M-bisV and TMAP-bisV by combined CV, diffusion-ordered spectroscopy (DOSY), and rotating disk electrode (RDE) experiments (Figure 2c–e)^[59] and the redox behaviors of M-bisV and TMAP-bisV were further elaborated. A near-linear relationship between peak current densities and root of potential scan rates was observed for M-bisV and TMAP-bisV (Figure 2c), indicating a diffusion-controlled process.^[63] The diffusion coefficient of M-bisV and TMAP-bisV as determined by DOSY experiments is 3.18×10^{-6} and $2.58 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$, respectively, lower than that of MV^[64] and BTMAP-Vi^[62] (5.7×10^{-6} and $3.07 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$), due to the increased molecular weights (Figure S8). The diffusion-controlled process was further verified by RDE studies (Figure 2d). The electron-transfer rate constants for M-bisV and TMAP-bisV as derived from RDE experiments are 1.30×10^{-2} and $1.60 \times 10^{-2} \text{ cm s}^{-1}$, respectively, which are significantly higher than that of MV^[64] and BTMAP-Vi^[62] (3.3×10^{-3} and $6.86 \times 10^{-3} \text{ cm s}^{-1}$, Figure 2f,g). We assume that the separate diradicals once generated will establish associative interactions and form intramolecular π dimers, thereby pushing away electrochemical equilibrium and accelerating the redox kinetics.

The π – π stacking of M-bisV and TMAP-bisV radicals was confirmed and studied by UV–vis and EPR spectra.

The UV–vis spectra for radicals of MV, BTMAP-Vi, M-bisV, and TMAP-bisV show distinct characteristics. The absorption of free monoradicals was observed at 602 and 600 nm for MV and BTMAP-Vi, whereas absorption peaks were observed at 534 and 834 nm for M-bisV and 532 and 838 nm for TMAP-bisV, a clear indication for the associative π – π stacking of radicals (Figures 3a and S9).^[52,56] By contrast, the associative π – π stacking of MV radicals and BTMAP-Vi radicals was only observable at a concentration up to 1 mM, with much lower absorbance intensity than that of M-bisV and TMAP-bisV (Figure S9e). We noticed a

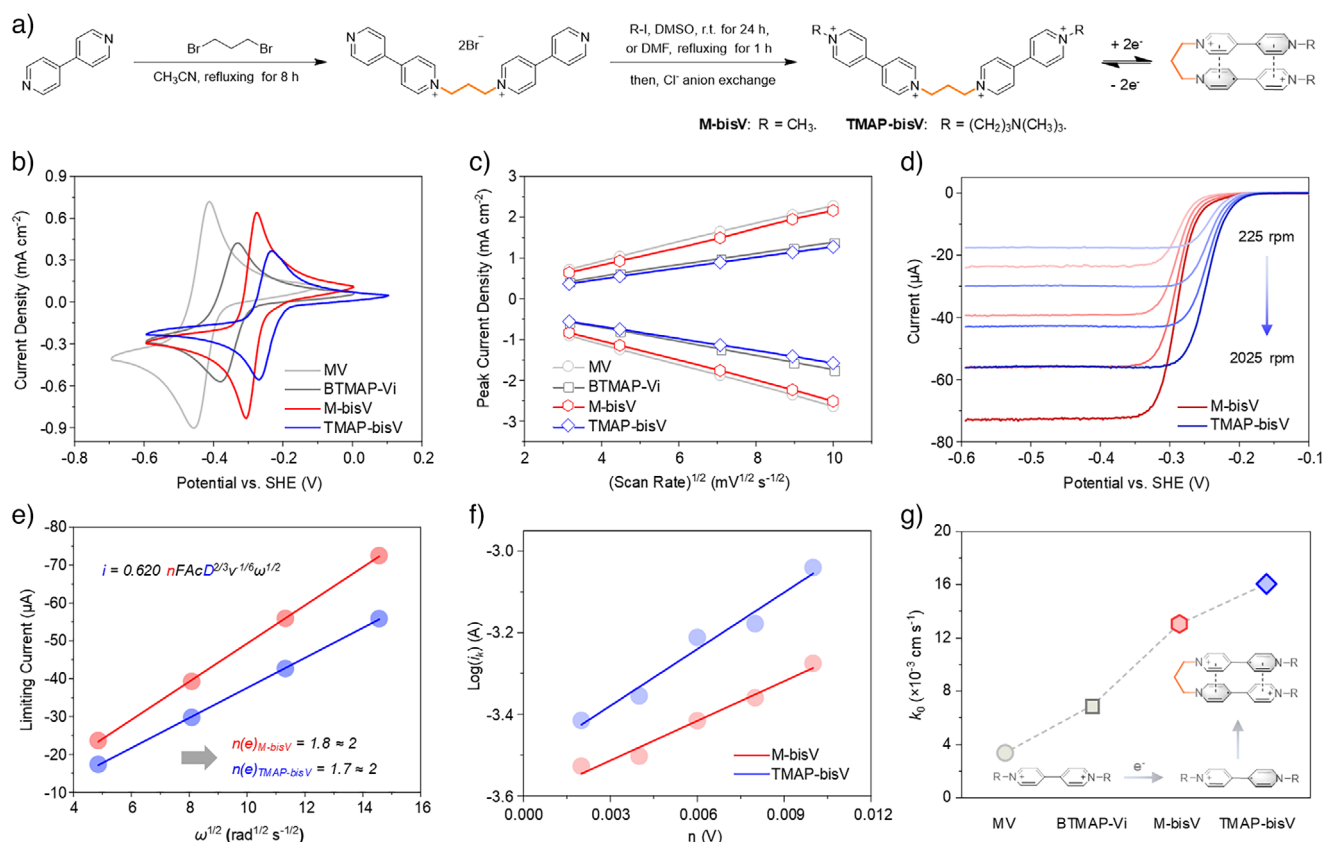


Figure 2. Synthesis and electrochemical properties of propylene-bridged bis(bipyridinium) electrolytes. a) Synthesis of M-bisV and TMAP-bisV. b) Cyclic voltammograms recorded at 10 mV s^{-1} , and c) peak current density at various voltage scan rates for M-bisV, TMAP-bisV, BTMAP-Vi, and MV at 10 mM e^- . d) Current as a function of potential during rotating disk electrode (RDE) experiments conducted on M-bisV and TMAP-bisV (1 mM e^-) at rotation rates from 225 to 2025 rpm with a potential sweeping rate of 5 mV s^{-1} . e) Levich plot of limiting current as a function of square roots of rotation rates indicates a two-electron transfer process for M-bisV and TMAP-bisV. f) Tafel plot, the logarithm of kinetically limited current versus overpotential (potential deviation from the formal reduction potential) for M-bisV and TMAP-bisV and g) the as-derived kinetic rate constant k_0 . Inset suggests a mechanism that the reduction of bis(bipyridinium) electrolytes may be accelerated by the formation of intramolecular π dimers.

linear relationship between absorbance intensity and radical concentration for bis(bipyridinium) radicals, suggesting a concentration-independent π - π stacking of M-bisV radicals and TMAP-bisV radicals (Figure 3b). Furthermore, the radicals of M-bisV and TMAP-bisV retained much stronger absorption intensity than that of MV and BTMAP-Vi after storing in a glovebox at 10 mM for 72 h, which may be attributed to the stabilizing effect of π - π stacking on radicals (Figure S9f).

Due to the detection limit of UV-vis, EPR studies were performed to reveal the π - π stacking of radicals at 100 mM (Figures 3c and S10). Because of the electrostatic repulsion of TMAP functional groups,^[65] BTMAP-Vi shows the highest relative radical intensity (normalized as 100%) in EPR spectra, whereas it is 89% for MV and decreases to 13% for M-bisV and 12% for TMAP-bisV. The EPR results are consistent with the UV-vis spectra studies (Figures S9 and S10), which reveal the preference for the radicals of M-bisV and TMAP-bisV to form associative π - π stacking interactions.

To unravel how the radicals of M-bisV and TMAP-bisV interact, we performed DFT calculations, optimized the molecular structure, and calculated ΔG of π - π stacking utilizing Gaussian, VMD, Shermo, and Multiwfn.^[66–69] Our

calculations reflect that π - π stacking of M-bisV radicals prefers to be intramolecular rather than intermolecular, with better overlapped highest occupied molecular orbital (HOMO) and more negative ΔG values for π - π stacking, as depicted in Figures 3d and S11.

As shown in Figure 3e, the DFT calculated ΔG values are 0.67 and $-14.36 \text{ kJ mol}^{-1}$ for the intermolecular π - π stacking of BTMAP-Vi and MV radicals, which sharply decrease to -101.49 and $-103.90 \text{ kJ mol}^{-1}$, respectively, for the intramolecular π - π stacking of M-bisV and TMAP-bisV radicals. Notably, the ΔG for the intramolecular π - π stacking of TMAP-bisV radicals is significantly lower than that of BTMAP-Vi. Considering their identical terminal groups, this indicates that our molecular design strategy can effectively facilitate the π - π stacking of radicals through associative intramolecular interactions. A similar trend is observed for M-bisV and MV. Then, we conducted DFT simulations to clarify multiple π - π stacking of MV and M-bisV. As shown in Figure S12a, the multiple π - π stacking of two MV π dimers is slightly favored^[52] with a ΔG value of $-2.25 \text{ kJ mol}^{-1}$, which is unfavored for M-bisV π dimers with a ΔG value of 2.20 kJ mol^{-1} , due to the steric hindrance of their terminal groups weakening π - π stacking (Figure S12b). Therefore,

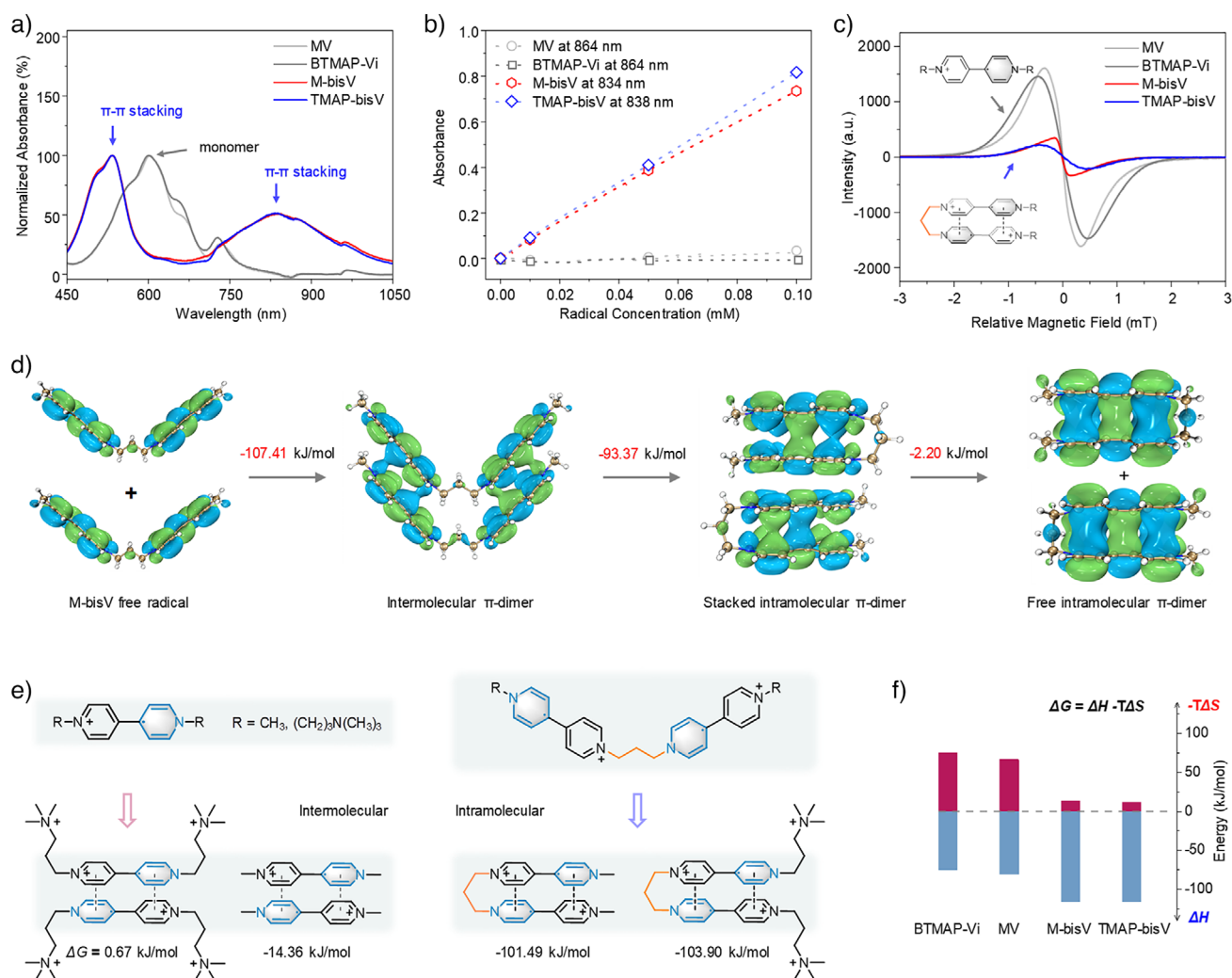


Figure 3. Intramolecular π - π stacking of M-bisV and TMAP-bisV. a) UV-vis spectra for the free radicals of MV, BTMAP-Vi, M-bisV, and TMAP-bisV at the same radical concentration of 0.01 mM, recorded in water. b) UV-vis absorbance at 834 nm and 838 nm (indication of the formation of intramolecular π dimeric structure) as a function of radical concentration for M-bisV and TMAP-bisV, respectively, compared with that of MV and BTMAP-Vi. c) Electron paramagnetic resonance spectra recorded at the same radical concentration of 0.1 M for MV, BTMAP-Vi, M-bisV, and TMAP-bisV (in 1 M NaCl). d) Molecular orbital structures and Gibbs free energy change analysis for the associative intramolecular π - π interaction for M-bisV. e) Gibbs free energy change and f) contributions of enthalpy (ΔH , blue) and entropy ($-\Delta S$, red).

the multiple π - π stacking of BTMAP-Vi and TMAP-bisV is blocked by their bulkier terminal groups.^[20,56]

Our calculations also show that the preferred intramolecular π - π stacking of M-bisV and TMAP-bisV radicals mainly stems from the limited entropic freedom of molecules (Figure 3f). DFT calculated ΔS for the π - π stacking of BTMAP-Vi and MV radicals is -0.25 and -0.22 kJ mol $^{-1}$ K $^{-1}$, respectively, as free bipyridinium radicals associate to form ordered π dimers. Nevertheless, by linking the radicals together, ΔS is merely -0.05 and -0.04 kJ mol $^{-1}$ K $^{-1}$ for M-bisV and TMAP-bisV radicals, respectively. To note, the calculated ΔH for the π - π stacking declines from -74.52 and -80.83 kJ mol $^{-1}$ for BTMAP-Vi and MV to -115.71 and -116.04 kJ mol $^{-1}$ for M-bisV and TMAP-bisV, respectively (Figure 3f). This suggests that the contribution of $-\Delta S$ plays a dominant role and this is because of the propylene linkage. The propylene bridge between bis(bipyridinium) radicals

could promote closer π - π stacking, with a N...N atom distance of 2.95 Å and 2.96 Å for M-bisV and TMAP-bisV, in comparison to that of 3.23 Å and 3.28 Å for BTMAP-Vi and MV, respectively (Figure S13a). As a result, HOMOs of bis(bipyridinium) radicals overlap better than that of free radicals, as depicted in Figure S13b.

Solubility and membrane permeation rates of M-bisV and TMAP-bisV were evaluated (Table 1). M-bisV shows solubility of 1.19 M in water and it increases to 1.24 M for TMAP-bisV, equivalent to a theoretical capacity density of 63.8 and 66.5 Ah L $^{-1}$, respectively. The permeability of M-bisV through a Selemion AMVN membrane (4.86×10^{-13} cm 2 s $^{-1}$) is two orders of magnitude lower than that of MV (1.19×10^{-11} cm 2 s $^{-1}$, Figures S14–S17), whereas it is even lower for TMAP-bisV (1.68×10^{-13} cm 2 s $^{-1}$). The results indicate that our molecular design strategy can effectively suppress the crossover

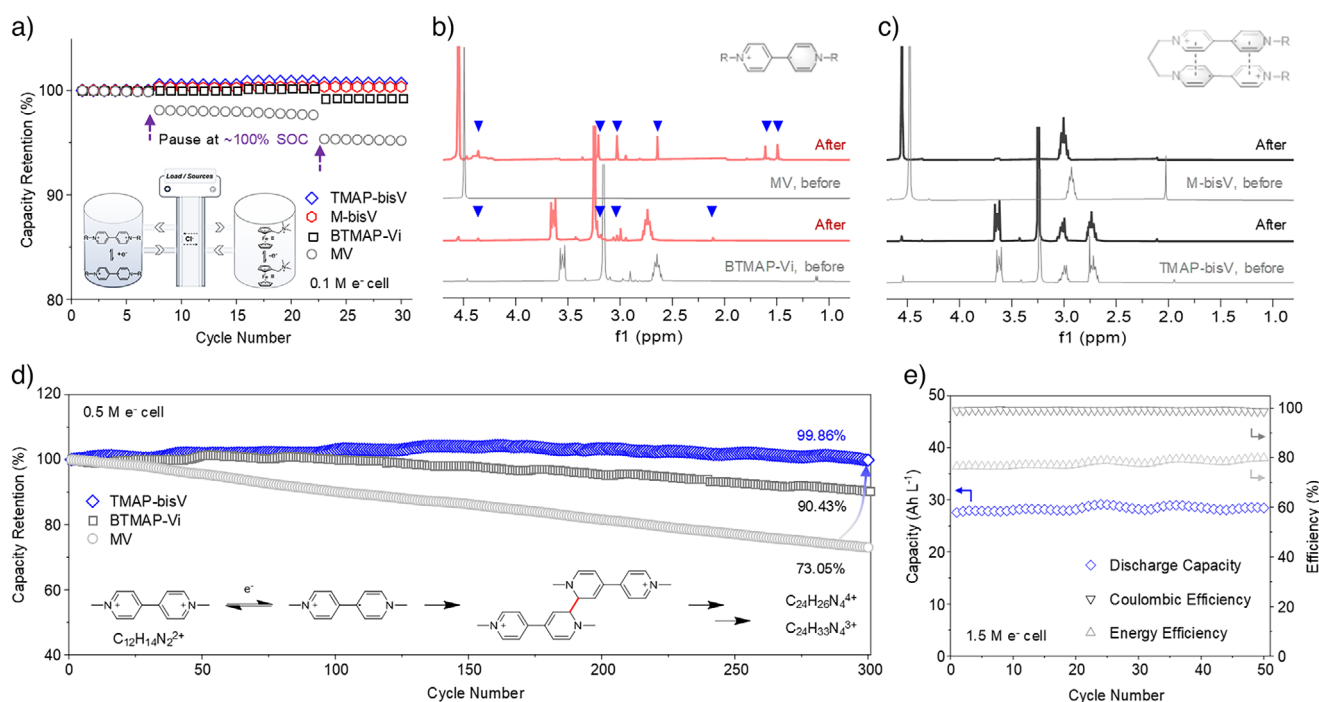


Figure 4. Cycling stability of flow cells assembled with electrolytes (MV, BTMAP-Vi, M-bisV, or TMAP-bisV) and a catholyte (FcNCl).^[37] a) Capacity retention as a function of cycle number during galvanostatic cycling of 0.1 M e⁻ MV, BTMAP-Vi, M-bisV, and TMAP-bisV at 30 mA cm⁻², with a potentiostatic hold at the end of charge and discharge. All cells are paused at ~100% state of charge (SOC) after the 7th and 22nd cycle for 12 h, respectively. Inset: the schematic of a flow cell assembled with bipyridiniums and FcNCl. ¹H-NMR spectra of b) MV and BTMAP-Vi and c) M-bisV and TMAP-bisV before and after battery cycling (mentioned above). d) Long-term galvanostatic cycling of 0.5 M e⁻ MV, BTMAP-Vi, and TMAP-bisV at 30 mA cm⁻² for 300 cycles (224–236 h), with a potentiostatic hold at discharge. Inset: the degradation mechanism of MV, identified by mass spectra. e) Long-term galvanostatic cycling of 1.5 M e⁻ TMAP-bisV at 30 mA cm⁻², with a potentiostatic hold at discharge. Discharge capacity, Coulombic efficiency (CE), and energy efficiency (EE) are plotted against the cycle number. The voltage cutoff is 1.0 V (or 1.1 V for the BTMAP-Vi-based cell, 1.2 V for the MV-based cell) during charge and 0.5 V during discharge. The potential hold is terminated until the current density is below 4 mA cm⁻².

of electrolytes and deliver concomitantly energy-dense AORFBs.

The stability of M-bisV and TMAP-bisV was rigorously evaluated. To do this, MV and BTMAP-Vi were selected as controls and they were paired with FcNCl^[37] (Figure S18), which is in excess and at an electron concentration of 0.1 M e⁻ (Figure 4a). A Selemon AMVN membrane was employed for cell assembly. Galvanostatic cycling was conducted at 30 mA cm⁻² with voltage cutoffs for charge at 1.0 V (or 1.1 V for BTMAP-Vi/FcNCl, 1.2 V for MV/FcNCl) and discharge at 0.5 V. To access the full capacity of the anolyte, a potentiostatic hold at the end of charge and discharge was applied until the current density dropped below 4 mA cm⁻². During cell cycling, the cells were deliberately paused at ~100% state of charge (SOC) after the 7th and 22nd cycle (or after the 15th cycle at ~0% SOC) for 12 h, respectively.

As shown in Figure 4a, the MV/FcNCl exhibited an obvious capacity fade during the whole cycling process, whereas a slight capacity fade was observed for BTMAP-Vi/FcNCl. The capacity fade mainly occurred during the pause at ~100% SOC, implying the vulnerability of radicals. By contrast, the capacity fade of M-bisV/FcNCl and TMAP-bisV/FcNCl was marginal, reflecting the enhanced anolyte stability. This suggests that designing bis(bipyridinium) electrolytes with associative intramolecular π - π stacking can alleviate side reactions caused by free radicals, thereby

enhancing battery cycling lifetime. We did not detect the crossover of electrolytes in postmortem analysis due to low cross-membrane permeability of electrolytes (Figures S19 and S20). We detected the degradation byproducts for the MV and BTMAP-Vi based cells, whereas those of M-bisV and TMAP-bisV were negligible (Figures 4b,c and S19). To note, degradation of FcNCl (although in excess) was also found.^[70] Additionally, the power density of M-bisV and TMAP-bisV based cells is comparable with that of MV and BTMAP-Vi based cells (Figure S21). Long-term continuous galvanostatic cycling of the above cells was conducted at 0.1 M e⁻ for 300 cycles. The M-bisV/FcNCl cell and TMAP-bisV/FcNCl cell exhibited much lower capacity fade rates of 0.00034% per cycle (or 0.042% per day) and 0.00010% per cycle (or 0.013% per day), in contrast to values of 0.0056% per cycle (or 0.72% per day) for MV/FcNCl and 0.00056% per cycle (or 0.071% per day) for BTMAP-Vi/FcNCl, respectively (Figure S21). Remarkably, the TMAP-bisV/FcNCl cell delivered the lowest capacity fade rate of 0.013% per day, projecting a decadal lifetime.

Continuous galvanostatic cycling of the above cells was also conducted at 0.5 M e⁻ and 1.5 M e⁻. At 0.5 M e⁻, the dynamic viscosity of anolyte solutions ranges from 1.074 to 1.635 mPa s⁻¹ (Figure S22). The TMAP-bisV/FcNCl cell demonstrated a capacity fade rate of merely 0.00047% per cycle (or 0.014% per day), whereas it was 0.0034% per cycle (or 0.10% per day) for M-bisV/FcNCl (Figure S23). The

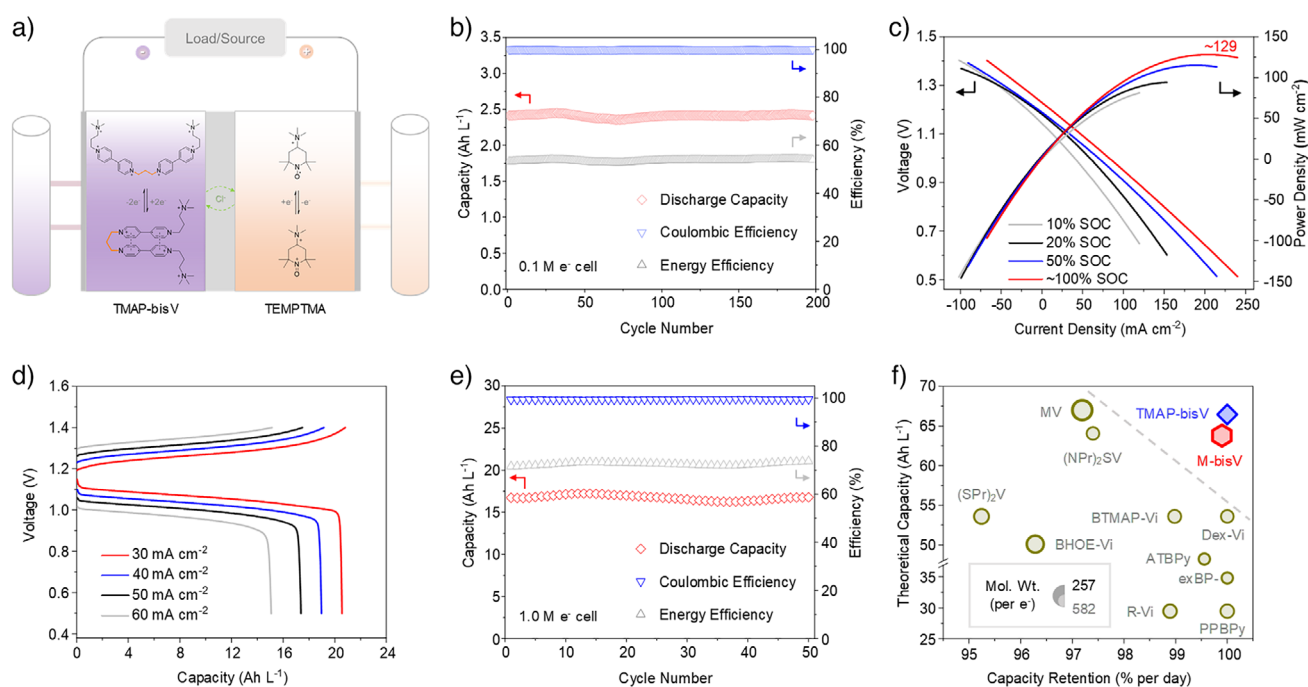


Figure 5. Performance of TMAP-bisV/TEMPTMA AORFBs. a) Schematics of a flow cell assembled with TMAP-bisV and TEMPTMA. b) Galvanostatic cycling of the 0.1 M e⁻ cell at 50 mA cm⁻², with a potentiostatic hold at the end of the discharge process until the current density is below 4 mA cm⁻². Discharge capacity, CE, and EE are plotted against the cycle number. The voltage cutoff is 1.5 V during charge and 0.5 V during discharge. Then, the performance of 1 M e⁻ cell was presented. c) Polarization curves and peak power densities at 10%, 20%, 50%, and ~100% SOC. d) Charge-discharge curves at current densities of 30, 40, 50, 60 mA cm⁻². e) Galvanostatic cycling of this cell at 50 mA cm⁻², with a potentiostatic hold at the end of the discharge process until the current density is below 4 mA cm⁻². Discharge capacity, CE, and EE are plotted against the cycle number. The voltage cutoff is 1.4 V during charge and 0.5 V during discharge. f) Comparing the theoretical capacity, capacity retention rate, and molecular weight per electron storage of M-bisV and TMAP-bisV with that of MV, (NPr)₂SV,^[71] (SPR)₂V,^[72,73] BTMAP-Vi, Dex-Vi,^[74] BHOE-Vi,^[62,75] ATBPY,^[76] exBP,^[20,59] R-Vi,^[73] and PPBPY.^[19]

control cells, BTMAP-Vi/FcNCl and MV/FcNCl, exhibited capacity fade rates of 0.032% per cycle (or 1.02% per day, in agreement with reports by Liang et al.^[57]) and 0.090% per cycle (or 2.81% per day), respectively. To note, the degradation of MV is significantly faster at 0.5 M mainly due to the formation of σ dimers as identified by mass spectra (Figure S24). Finally, at 1.5 M e⁻, the TMAP-bisV/FcNCl cell demonstrated a high capacity of 27.6 Ah L⁻¹, and no capacity fade was observed during continuous cycling (Figure 4e). Our results reveal an interesting fact that the degradation of bis(bipyridinium) electrolytes is concentration irrelevant, which stands in direct contrast to previous observations on bipyridinium electrolytes whose degradation is strongly concentration-dependent.^[16] The result highlights the unique advantage of designing bis(bipyridinium) electrolytes and promoting associative intramolecular π - π stacking in our strategy.

The relatively low redox potential and sluggish kinetics of FcNCl may limit the power density and charge-discharge voltage of the TMAP-bisV/FcNCl cells (Figure S21).^[37] Therefore, TEMPTMA, with a higher redox potential of 0.93 V versus SHE and a greater k_0 of 4.2×10^{-3} cm s⁻¹, was adopted (Figure 5a).^[43,64] When paired with TEMPTMA, the TMAP-bisV/TEMPTMA cell assembled at 0.1 M e⁻ exhibited no capacity loss during continuous cell cycling (Figure 5b). The 1 M e⁻ cell can deliver a peak power density

of ~129 mW cm⁻² at ~100% SOC, a discharge voltage of ~1.1 V, and an experimental capacity of 20.8 Ah L⁻¹ at 30 mA cm⁻² (Figure 5c,d). No obvious capacity fade is observed during continuous cell cycling (Figure 5e). Notably, M-bisV and TMAP-bisV could deliver concomitant highly stable and energy-dense batteries at a low molecular weight of 263 or 383 per electron and a theoretical capacity of 63.8 or 66.5 Ah L⁻¹, respectively, which represents an obvious advance over reported bipyridiniums (Figure 5f and Table S1). We believe that the proposed strategy of designing covalently bridged radicals with associative intramolecular π - π stacking may promote the development of other organic molecules for AORFBs and stable radicals in other areas.

Conclusion

In summary, this work introduces a strategy for designing associative bis(bipyridinium) electrolytes, which promotes the intramolecular π - π stacking of redox-active bipyridinium moieties and significantly enhances battery stability. This concept was exemplified by two bis(bipyridinium) electrolytes, namely M-bisV and TMAP-bisV, in which two bipyridinium moieties are combined by a propylene bridge. We elaborated on the preferred π - π stacking behaviors of bis(bipyridinium) radicals using CV, UV-vis, and EPR studies. To understand

the radical π - π stacking, we conducted DFT calculations to reveal the driving force for the intramolecular π - π stacking of bis(bipyridinium) radicals, and we found that the limit of molecule freedom contributed mainly to the lower ΔG for intramolecular associative binding. In the 0.5 M e^- flow cells, M-bisV and TMAP-bisV exhibited much lower capacity fade rates of 0.10% and 0.014% per day, respectively, when compared with MV (2.81% per day) and BTMPA-Vi (1.02% per day). This strategy renders M-bisV and TMAP-bisV a high theoretical capacity of 63.8 and 66.5 Ah L⁻¹, respectively, at a molecular weight of 263 and 383 per electron stored, which is comparable to the simplest form of bipyridinium electrolytes (MV) and significantly superior to others. Impressively, TMAP-bisV possesses a theoretical capacity of 66.5 Ah L⁻¹ and demonstrated negligible capacity fade at an electron concentration of up to 1.5 M, representing a benchmark for energy-dense and long-life pH-neutral AORFBs. We believe that our strategy can benefit the exploration of organic electrolytes for AORFBs and stable radicals for other areas, by regulating the intramolecular or intermolecular associative interactions.

Author Contributions

Tongwen Xu and Zhengjin Yang supervised this work. Zhengjin Yang and Gonggen Tang conceived this project and wrote the paper. Gonggen Tang performed all the experiments and data analysis. Kang Peng, Yahua Liu, and Junkai Fang contributed to data curation, analysis, presentation, and discussion. Gonggen Tang and Wenyi Wu carried out DFT calculations.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Aqueous organic redox flow battery • Bipyridinium electrolyte • Energy storage • Radical • π -dimer

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